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THEORETICAL STUDIES IN MOLECULAR FRAGMENTATION:
PROCESSES, ENERGISTICS AND DIAGNOSTICS(U) SMITHSONIAN
ASTROPHYSICAL OBSERVATORY CAMBRIDGE MA K P KIRBY

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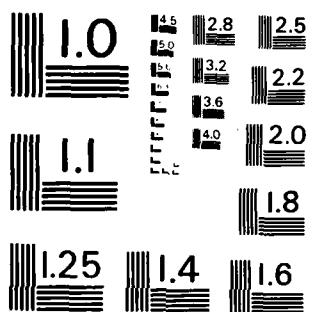
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Molecular structure; radiative lifetimes; configuration interaction wavefunctions.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Calculations of excited state potential energy curves and radiative lifetimes of CH and NH have been carried out in order to provide diagnostic data with which to identify and quantify the presence of product fragments resulting from the rapid decomposition of energetic materials. Large basis configuration interaction wavefunctions have been employed to obtain a high level of accuracy which will complement experimental measurements.

21. SUBJECT TERMS (Continue on reverse side if necessary and identify by block number)

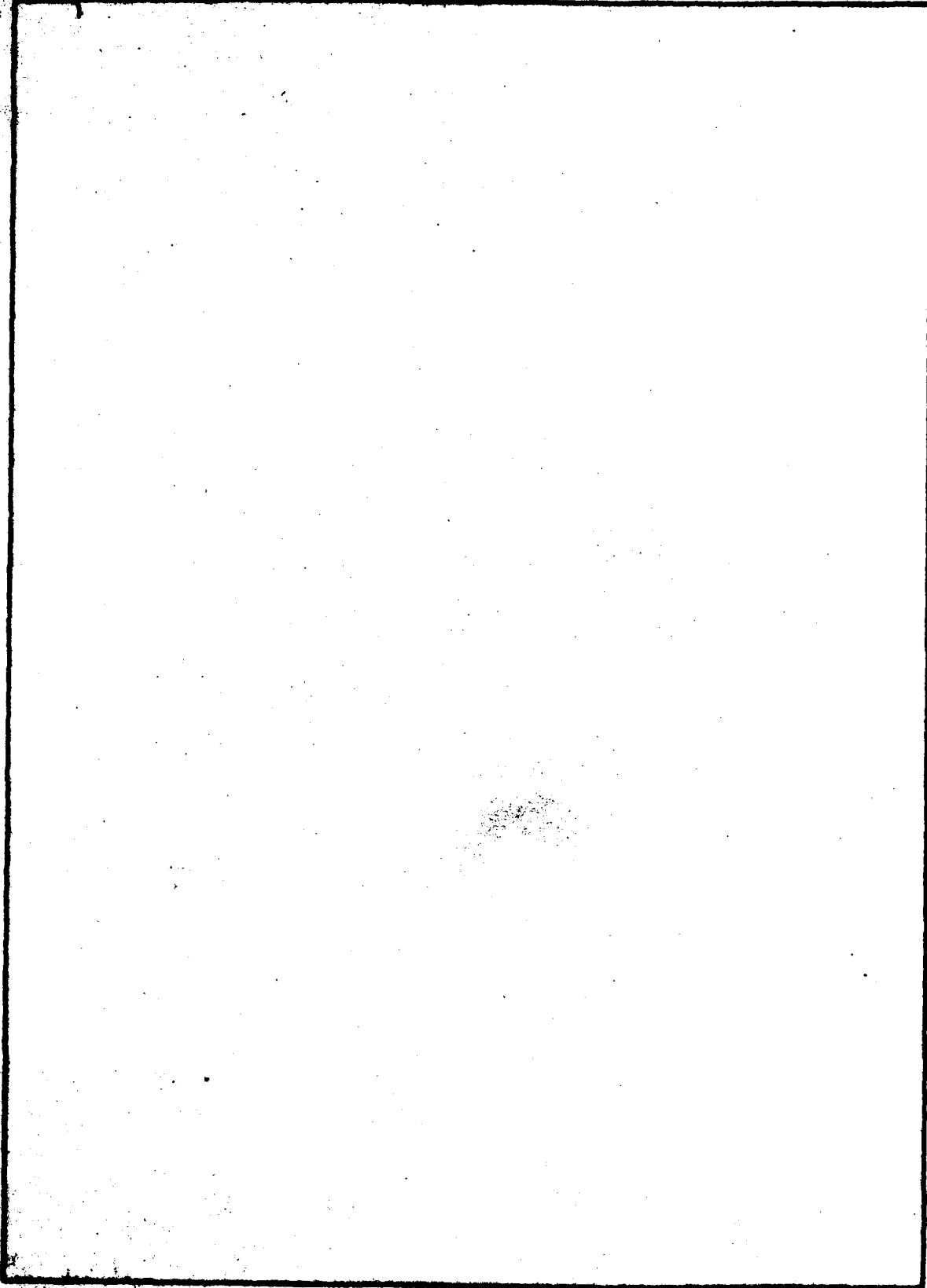
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THEORETICAL STUDIES IN MOLECULAR FRAGMENTATION:
PROCESSES, ENERGETICS AND DIAGNOSTICS

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In order to provide diagnostic data with which to identify and quantify the presence of molecular fragments resulting from the destruction of highly energetic materials, we have continued our ab initio calculations of excited electronic states and radiative lifetimes of the small diatomic fragments CO and NH. Such calculations are designed to complement experimental spectroscopic measurements, providing data which cannot be easily obtained in the laboratory.

We have identified particular excited states in both the CO and NH molecules which appeared to be important as possible origins of as yet unobserved band spectra or as possible photodissociation or predissociation channels. In addition to characterizing the complete potential curves as a function of internuclear separation, we also will be calculating excited state radiative lifetimes.

In CO we have chosen to examine the four lowest-lying excited states in the 1Π and $1\Sigma^+$ manifolds, and have devised a series of calculations to obtain potential energy curves and wavefunctions at internuclear separations ranging from $R=1.5a_0$ to $R=20a_0$. The excited states of 1Π and $1\Sigma^+$ symmetry contain substantial amounts of Rydberg character at short internuclear distances and the configuration interaction wavefunctions which we construct must be capable of describing valence-Rydberg mixing.

First, a full-valence multi-configuration self-consistent field (FVMSCF) calculation is performed for the lowest 1Π



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state. The 1σ and 2σ orbitals are always doubly occupied and the valence orbital space consists of $3\sigma - 6\sigma$, 1π and 2π . The MCSCF orbitals are then used in a single excitation configuration interaction (CI) calculation to generate a set of natural orbitals, from which one can choose the lowest energy Rydberg molecular orbitals. The valence orbitals as well as the Rydberg molecular orbitals are then used in a large CI calculation which includes configurations in the full valence space, single excitations from the full valence space into both the Rydberg orbitals (7σ and 3π) and the full set of virtual orbitals ($8\sigma-32\sigma$, $4\pi-18\pi$, 6δ), and simultaneous single excitations into the Rydberg and virtual spaces. The simultaneous single excitations are necessary to allow the core to relax to a CO^+ description while the Rydberg orbital is occupied. The large CI wavefunctions consist of 47,036 configuration state functions (CSF's) for $^1\Pi$ symmetry and 26,951 CSF's for $^1\Sigma^+$ symmetry.

We calculate energies and wavefunctions for 4 states of each symmetry, and the computer time (IBM 3033) required is 3 hours for the $^1\Pi$ calculation and 2 hours for the $^1\Sigma^+$ calculation. In order to stretch our computing dollars we carry out these c.p.u. intensive calculations only on weekends when the rates for computer time are 25% of the usual rates. Because of this limitation, progress is slow. However, from the five points which we have computed it appears that our calculations are in excellent agreement with available spectroscopic measure-

ments which appear in parentheses: $T_e(A^1\Pi-X^1\Sigma^+) = 8.27\text{eV}$ (8.07eV), $T_e(B^1\Sigma^+-X^1\Sigma^+) = 10.53\text{eV}$ (10.78eV), and $T_e(2^1\Pi-X^1\Sigma^+) = 11.27\text{eV}$ (11.52eV). The dissociation energies for the $A^1\Pi$ and $X^1\Sigma^+$ states are 2.77eV and 10.97eV compared to experimental values of 3.17 and 11.24eV, respectively.

The first two states of each symmetry are energy degenerate asymptotically, and dissociate to $C(^3P) + O(^3P)$. We obtain this degeneracy to better than .03eV at $R=8.0a_0$. The third and fourth roots of each symmetry are also energy degenerate, separating to $C(^1D) + O(^1D)$ at 3.23eV (exact) above the ground state atoms. Our excited atom asymptotes are split by ~.1eV and lie ~3.6eV above the ground state atoms.

We have completed calculations of the potential curves and dipole moments of the four lowest states of $^3\Sigma^-$ symmetry in NH (ground state, $X^3\Sigma^-$). There is only one published calculation on the second $^3\Sigma^-$ state which was not of high quality. Our calculations indicate that the state is repulsive and may be an important pathway in the photodissociation of NH. The third and fourth $^3\Sigma^-$ states have never before been characterized, and appear to be bound states which dissociate to $N(^4S) + H(2s,2p)$. Rydberg-valence mixing is very important for an adequate description of these three excited states; and our atomic basis set of Slater-type functions include diffuse functions on both N and H.

In much the same manner as described for CO, we obtain valence molecular orbitals ($2\sigma - 4\sigma, 1\pi$) from a full valence MCSCF calculation on the $X^3\Sigma^-$, and Rydberg molecular orbitals

from a single excitation CI calculation. A number of exploratory calculations were performed in order to understand the types of configurations necessary to obtain a balanced description of both the ground and excited states, and to allow the states to dissociate properly asymptotically. We concluded that an accurate calculation of these four states would have to include some double excitations for a proper description of the X state bonding, and would have to treat the Rydberg and valence orbitals equivalently as much as possible.

In order to include some double excitations (a complete set of double excitations would have been prohibitive) we used the most highly occupied natural orbitals (5 σ 's, 4 π 's, and 2 δ 's) obtained from a pairwise double excitation CI calculation for a doubles space. Our final CI wavefunction consisted of two internal spaces containing four valence and four Rydberg orbitals, and two external spaces formed from the doubles space and the remaining virtual orbitals. The final CI wavefunction has almost 23,000 CSF's.

We obtain a ground state energy which is close (.17eV) to the full singles and doubles result and a satisfactory $D_e = 3.29\text{eV}$ (3.41eV, experimental). Excitation energies to the excited states are $T_e = 9.6\text{eV}$, 10.56eV, and 11.08eV, and dipole moments from the $X^3\Sigma^-$ state are in good agreement with those obtained from other accurate calculations. The asymptotic energy splitting between the $N(^2D) + (H(^2S))$ limit and

the ground state atoms $N(^4S) + H(^2S)$ is 2.64eV (2.33eV, experimental), reflecting the fact that orbitals were optimized for $N(^4S)$ and not $N(^2D)$. The asymptotic energy splitting for the $N(^4S) + H(2s, 2p)$ roots is 10.29eV (10.20eV, experimental), reflecting the residual difference in treatment of the valence and Rydberg orbitals in the large CI wavefunction.

Publications and Talks

"Oscillator strengths for infrared vibration-rotation transitions of CN and applications to cometary resonance fluorescence", G. Lafyatis, J. Black and K. Kirby, to be submitted to Astrophysical Journal.

"Potential Energy Curves for the Four Lowest $^3\Sigma^-$ States of NH", E.M. Goldfield and K. Kirby, a talk to be given at the fifth American Conference on Theoretical Chemistry in Jackson Hole, Wyoming, June 15-June 20, 1984.